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(54) Improved durability metallic-ceramic turbine air seals.

(57) An improved durability turbine air seal comprises a metallic substrate, a metallic bond coat on the substrate, a continuously graded metal-ceramic layer on the bond coat and an outer layer of pure ceramic. The continuously graded metal-ceramic layer consists of a ceramic material having a reduced oxygen permeability compared to the zirconia material used in the prior art and a metallic material having a high resistance to oxidation. The seal is fabricated by plasma spraying with controlled subtrate temperatures to induce in the sample a controlled strain distribution so as to make the seal resistant to failure in service. Other concepts for reducing the liability of the seal to failure by oxidation are described.

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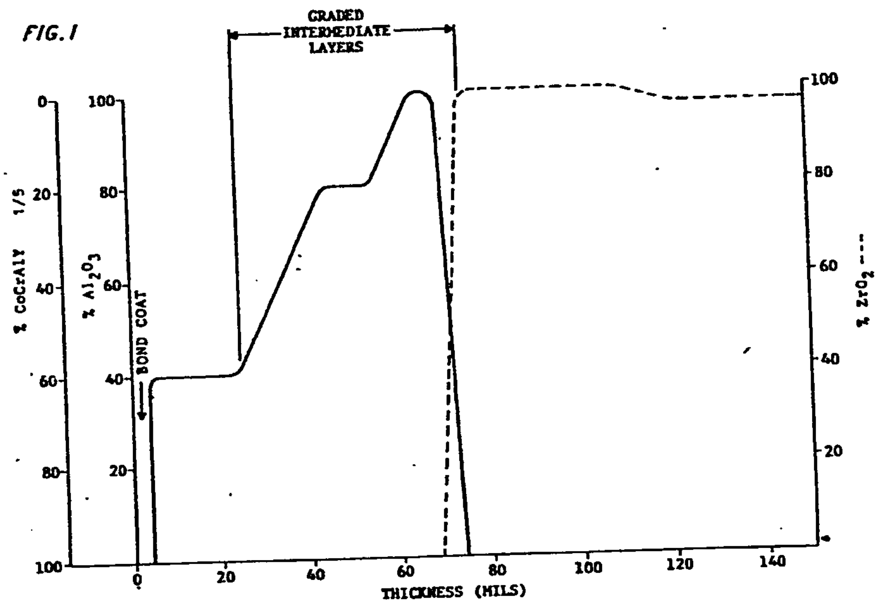
FIG. I


GRADED
INTERMEDIATE
LAYERS
% CoCrAlY 1/5
% Al_2O_3
BOND COAT
% ZrO_2
0
20
40
60
80
100
120
140
THICKNESS (MILS)

Description

Improved Durability Metallic-Ceramic Graded Turbine Air Seals

Technical Field

The field of the invention is that of gas turbine engine air seals and also the field of plasma spraying of mixed metal-ceramic materials.

Background Art

In modern gas turbine engines working medium gases having temperatures in excess of 2,000°F are expanded across rows of turbine blading for extraction of power therefrom. A shroud, termed an outer air seal, circumscribes each row of turbine blading to inhibit the leakage of working medium gases over the blade tips. The limitation of the leakage of the working medium gases is crucial to the achievement of high efficiencies in such engines. The graded ceramic seals described herein were developed for specific application in gas turbine outer air seals, although other applications are clearly possible. Durable seals capable of long-term, reliable service in the hostile turbine environment were required. Specifically sought were high temperature capability and good resistance to thermal shock. In addition, the seal material must have

adequate surface abradability to prevent destructive interference upon occurrence of rubbing contact of the seals by the circumscribed turbine blading.

U.S. Patent Nos. 3,091,548 to Dillion entitled "High Temperature Coatings"; 3,879,831 to Rigney et al entitled "Nickel Base High Temperature Abradable Material"; 3,911,891 to Dowell entitled "Coating for Metal Surfaces and Method for Application"; 3,918,925 to McComas entitled "Abradable Seal"; 3,975,165 to Elbert et al entitled "Graded Metal-to-Ceramic Structure for High Temperature Abradable Seal Applications and a Method of Producing Same" and 4,109,031 to Marscher entitled "Stress Relief of Metal-Ceramic Gas Turbine Seals" are representative of the known concepts applicable to ceramic faced seals.

As is discussed in some of the above references and in particular detail in U.S. Patent No. 4,163,071 to Weatherly et al entitled "Method for Forming Hard Wear-Resistant Coatings", the temperature of the metallic substrate to which the ceramic coating is applied may be preheated to control either residual stress or coating density. Generally, such heating has been to a uniform temperature. U.S. Patent No. 4,481,237 of common assignee with the present application, describes the production of discrete layered turbine seals wherein the seal is produced by plasma spraying

discrete layers of essentially fixed composition on a metallic substrate while simultaneously varying the substrate temperature. U.S. Patent Application Serial No. 675 806 filed on even date herewith, broadens the concept and describes methods of continuous grading of mixed metal-ceramic materials.

Although many of the materials and methods described in the above patents are known to be highly desirable, the structures resulting therefrom have yet to achieve full potential, particularly in hostile environment applications. Significant research into yet improved materials and methods continues.

Disclosure of Invention

According to the present invention, discrete graded layer seals of the type described in U.S. Patent No. 4,481,237 or continuously graded metal-ceramic seals of the type described in copending U.S. Application Serial No. 675 806 "Method for Producing Continuously Graded Air Seals", filed on even date herewith, are afforded substantially enhanced performance by employing as a ceramic material in the graded portion, a material having a low oxygen permeability at elevated temperatures such as alumina, mullite, or the $MgO \cdot Al_2O_3$ spinel.

Additionally, oxidation resistant metallic materials are employed, particularly

those of the MCrAlY type (where M is Fe, Ni or Co) and related materials.

Other concepts are described for enhancing the durability of mixed metal-ceramic seal systems. One such method involves reducing the surface area of the metallic constituent by either limiting the powder size to be relatively coarse and uniform (i.e., reducing the high surface area fine particle content) and/or employing plasma deposition parameters under which the metallic constituent does not melt completely so that upon impact it remains in a rounded form rather than assuming a high surface area splat configuration. Another approach is to preoxidize the metallic constituent.

The final concept relates to minimizing the swelling resulting from oxidation of the metallic constituent by deliberately inducing porosity into the material by cospraying a fugitive material along with the metallic-ceramic material.

In addition to the specific details relating to the mixed metal-ceramic layer, the invention also teaches the use of a thin 100% alumina layer on the mixed layer for purposes of affording total resistance to oxygen penetration and the use of a abradable ceramic layer such as zirconia as the outer seal constituent to provide abradable rubbing contact upon interaction with the moving turbine blading and to provide improved temperature capabilities.

The foregoing features and advantages of the present invention will be made more evident in light of the following description of the best mode for carrying out the invention and the accompanying drawings.

Brief Description of Drawings

Figure 1 shows the composition profile for a seal according to the invention;

Figure 2 is a photomicrograph (25X) of a turbine air seal;

Figure 3 shows a schematic illustration of a turbine air seal;

Figure 4 shows the variation in substrate temperature during deposition of the seal according to Figure 1; and

Figure 5 shows the oxygen permeability of zirconia and alumina.

Best Mode for Carrying Out the Invention

The requirements for producing a successful graded metal-ceramic seal may be organized in two categories. The first is the physical requirements of the seal, particularly composition. The second relates to the residual strain which may be built into the system through control of substrate temperature during plasma deposition. This invention is directed at the first category, namely, the physical properties of the graded metal-ceramic layer. Aspects of the second category, namely the

control of residual strain will be described as necessary to permit an understanding of the best mode of practicing the invention. These strain control aspects are described in U.S. Patent No. 4,481,237 (which is incorporated herein by reference) for the discrete layer case and in U.S. Patent Application Serial No. 675 806 filed on even date herewith (which is incorporated herein by reference) for the case of continuous grading.

Figure 1 illustrates the composition versus thickness of the best seal known to the inventors at the time of the filing of this application. Starting from the substrate and going outwards, the X axis shows seal thickness in mils and the total seal thickness is approximately 150 mils. Since the seal is deposited by a plasma deposition, the seal thickness will actually vary in a stepwise fashion from one layer to the next, however, since each layer is in the order of 1 mil thick the continuous curve of Figure 1 is a more than adequate description of the seal composition.

Starting from the substrate there is an initial metallic bond coat of a composition known as Metco 443 which is a commercially available material formed from an agglomeration of nickel chromium powder and aluminum powder which upon plasma spraying undergoes an exothermic reaction which is believed to aid in the adherence of the bond coat to the substrate.

Following the deposition of the bond coat the next 20 mils are of a constant composition of 60% CoCrAlY (nominal composition of Co-23Cr-13Al-0.65Y) having a particle size of -100+325 U.S. Standard Sieve and 40% alumina. Following the deposition of this constant composition layer, continuous grading occurs over the next 25 mils or so until a composition of 20% CoCrAlY and 80% alumina is reached. This composition is maintained constant for about 10 mils then the grading process continues until a composition of 100% alumina is achieved. One layer (1$\pm$.5 mil) of 100% alumina is then deposited, it has been found that the absence of all alumina layer detracts from oxidation performance but that multiple layers are detrimental to mechanical behavior. Finally an outer layer of zirconia is applied to provide abradability and temperature capability (Al_2O_3 melts at ~2000°C while ZrO_2 melts at ~2700°C). Alumina is a harder, stronger material than zirconia and alumina as the outer layer would not have the desired abradable qualities. To further increase the abradability of the zirconia deliberate porosity is induced in the zirconia in the outer portion thereof, porosity on the order of about 19%. This is accomplished by adding a fugitive material (such as Metco 600 polyester or DuPont's Lucite®), to the ceramic material and subsequently removing the fugitive by baking at a high temperature to vaporize the

fugitive material. Accordingly, Figure 1 describes in some detail the apparent physical characteristics of a preferred embodiment of the present invention. It should also be apparent that the various details of the present invention could be readily applied to the discrete layered system described in U.S. Patent No. 4,481,237.

Figure 2 is a photomicrograph of the resultant structure. The metallic constituent is light in color, the alumina is dark gray, the zirconia is light gray and the porosity is black.

Figure 3 is a schematic of a turbine air seal showing the arrangement or layers, the plasma torch and the substrate heating.

Figure 4 illustrates the temperature control of the substrate which is employed during plasma spraying to attain the desired and necessary substrate prestrain conditions. The substrate temperature is maintained at a relatively high level during deposition of the bond coat and is then reduced. Thereafter the substrate temperature is increased generally in parallel with the ceramic content and eventually reaches a level above that employed during deposition of the bond coat and then tapers off during the deposition of the outer abradable ceramic material.

A primary aspect of this invention is the substitution of a material which is resistant to

the diffusion of oxygen at elevated temperatures. Three such materials have been identified for seal application. These are alumina, mullite and the $MgO \cdot Al_2O_3$ spinel.

Figure 5 shows the permeability of stabilized zirconia and alumina over a temperature range at 50 Torr partial pressure of oxygen. It can be seen that at 1600°C the permeability of oxygen in alumina is less than about 10^{-10} and it is about 3 orders of magnitude less than the permeability of oxygen in zirconia at the same temperature. The other suggested materials, mullite and the spinell, both have oxygen permeability which are less than 10% of that of zirconia at elevated temperatures.

Additionally, oxidation resistant materialselected from the group consisting of the MCr materials where chromium ranges from about 20 to about 40%; the MCrAl materials where chromium ranges from about 15 to about 45% and aluminum ranges from about 7 to about 15%; the MCrAlY materials where chromium ranges from about 15 to about 45%, aluminum ranges from about 6 to about 20% and yttrium ranges from about 0.1 to about 5%; and the MCrAlHf materials where chromium ranges from about 15 to about 45%, aluminum ranges from about 7 to about 15% and hafnium ranges from about 0.5 to about 7% In all of these materials "M" is selected from the group consisting of nickel, cobalt,iron and

mixtures thereof with mixtures of nickel and cobalt being particularly favored, the yttrium (when present) may be partly or wholly replaced by lanthanum, cerium, Misch metal and mixtures thereof, additionally, up to 10% of a material selected from the group consisting of platinum, tungsten, rhenium, silicon, tantalum and manganese may be added to any of these materials are utilized.

Table I presents oxidation data for two compositions based on ceramic-CoCrAlY materials. In one composition the ceramic is zirconia and the other the ceramic is alumina, in both compositions the CoCrAlY content was the same volume percent. These materials were tested at 1900°F for 150 hours. The results are presented in the table. It can be seen that the zirconia base material gained 3.3% in weight due to oxidation of the metallic constituent and underwent a longitudinal expansion of 3.4% due to swelling of the material caused by the oxidation of the metallic constituent. Under the same condition the alumina based material gained 2.1% in weight, (a reduction of 37% compared to the zirconia based material), and shrank 0.5% in length. The information in Table I supports the basic premise of the invention which that the substitution of alumina for the commonly used zirconia material in mixed metal-ceramic systems provides substantial seal performance benefits.

Table I

1900°F/150HRS

	Δwt,%	Δℓ,%
85%ZrO_2/15%CoCrAlY	3.3	3.4
80%Al_2O_3/20%CoCrAlY	2.1	-.5

Table II shows the benefit obtained through minimizing the surface area of the metallic constituent by sieving out the fine particles. In Table II both compositions were based on the zirconia ceramic which serves as a valid baseline for demonstrating the benefits obtained by employing coarse particles. Table II shows the weight change results of two materials both of which had the same composition of 85% zirconia, 15% CoCrAlY, the difference between the two samples being that one was produced from a wide size range metallic powder composition of -100+325 mesh while the other was produced from metallic material having -100+200 mesh (the mesh sizes referred to are those described in the U.S. Standard Sieve Series; -100 describes all those particles which will pass through a wire mesh having square openings .149 millimeters on a side, +325 mesh means that the material will be retained on a wire mesh having average

openings of .044 millimeters and +200 mesh means the material will be retained on a mesh having an average opening of .074 millimeters on a side). Thus the essential difference between the two compositions is that the particles which would pass through the 200 mesh screen were rejected in the second composition but were retained in the first composition. From Table II it is clear that the elimination of fine particles plays a significant role in reducing weight change due to oxidation. In this experiment the dimensional changes were not evaluated.

Table II

1650°F/24HRS

	Wt Change
85%ZrO_2/15%CoCrAlY -100+325	8.4 mg/cm^2
85%ZrO_2/15%CoCrAlY -100+200	4.8 mg/cm^2

Very preliminary experiments were performed using CoCrAlY material which had been deliberately preoxidized for about 6 hours at about 400°F to produce an alumina layer on the surface of the powder which would serve to retard further oxidation. It appears from the very preliminary work done that a reduction in

oxidation of about 20% can be achieved through this technique.

Table III presents basic information on the effect of including deliberate porosity on the performance of alumina-CoCrAlY composites produced by plasma spraying. From Table III it is evident that material which contained 4% polyester and therefore contains some amount of porosity (about 2%) exhibited slightly increased weight change due to oxidation but rather significantly decreased dimensional changes. Thus, the deliberate inclusion of porosity is an area which will require careful attention by the skilled artisan.

Table III

1900°F/150HRS

	Δwt,%	$\Delta \ell$,%
80%Al_2O_3/20%CoCrAlY	2.1	-.5
76%Al_2O_3/20%CoCrAlY/4%Polyester	2.2	-.3

The final suggested technique for reducing oxidation and resultant swelling is to perform the plasma spraying under conditions which do not entirely melt the metallic constituent so that the metallic constituent will retain a more nearly spheroidal configuration within the

graded coating rather than assuming a completely flattened splat configuration which will result if total melting occurs. Observed aspect ratios (length:thickness) in totally melted materials are from about 5:1 to about 10:1, reduced surface areas result when aspect ratios of about 3:1 or less are produced. This result may be accomplished by adjusting the position within the plasma torch where the metallic constituent is injected so that the metallic constituent has a short residence time within the plasma zone and does not melt completely. The use of coarse particles also assists in controlling aspect ratio.

The effective commercial production of the graded seal described in Figures 1 and 2 at the beginning of this section requires some refined plasma spraying techniques which are not known in the art and which are the subject of commonly assigned U.S. Patent Applications Serial Nos. 675 801 and 675 806 filed on even date herewith which are all incorporated by reference. U.S. Patent Application Serial No. 675 806 describes the temperature management schemes, for continuously graded coatings, which were previously mentioned with respect to Figure 1 and which produce the necessary prestrain in the coating which permit the coating to withstand severe conditions at elevated temperatures without spallation. U.S. Patent Application Serial No. 675 807 deals with a

plasma spray powder management system which has been employed to produce the mixed powder combinations in a highly controllable and reproducible fashion. The essentials of the system are accurate measurements of carrier gas flow and pressure coupled with x-ray measurements of the gas plus powder stream, these measurements are supplied to a controlling microcomputer which generates signals necessary to control the flow of gas and the flow of the various powders. U.S. Patent Application Serial No. 675 801 deals with the powder flow gauging techniques which are used to measure the actual powder streams and to control their flow Briefly, the x-ray gauging system uses flow and pressure sensors to provide accurate measurements of carrier gas flow and uses a transmission x-ray apparatus to give an indication of the total mass flow of powder plus carrier gas. From these measurements the mass flow rate can be accurately calculated. Knowing the actual powder mass flow rate one can employ control circuitry to control and constrain the powder flow rate to follow a predetermined schedule.

Although this invention has been shown and described with respect to preferred embodiments, it will be understood by those skilled in this art that various changes in form and detail thereof may be made without departing from the spirit and scope of the invention.

Claims

1. In a graded metal-ceramic structure of the type in which the composition varies from essentially 100% metal at one interface to essentially 100% ceramic at a second interface, and in which the stress state of the graded layer varies through its thickness, the improvement which comprises:

employing a ceramic material having an elevated temperature oxygen permeability constant which is less than about 10% of that of ZrO_2 as the ceramic constituent so that the metallic constituent is isolated and protected from oxygen and is thereby rendered more durable at elevated temperature under oxidizing conditions.

2. A structure as in Claim 1 in which the ceramic is selected from the group consisting of alumina (Al_2O_3), mullite ($3Al_2O_3 \cdot 2SiO_2$) and $MgO \cdot Al_2O_3$ spinel and mixtures thereof.

3. A structure as in Claim 1 in which the metallic constituent is selected from the group consisting of the MCr materials where chromium ranges from about 20 to about 40%; the MCrAl materials where chromium ranges from about 15 to about 45% and aluminum ranges from about 7 to about 15%; the MCrAlY materials where chromium

ranges from about 15 to about 45%, aluminum ranges from about 7 to about 20% and yttrium ranges from about 0.1 to about 5%; and the MCrAlHf materials where chromium ranges from about 15 to about 45%, aluminum ranges from about 7 to about 15% and hafnium ranges from about 0.5 to about 7% in all of these materials "M" is selected from the group consisting of nickel, cobalt,iron and mixtures thereof with mixtures of nickel and cobalt being particularly favored, the yttrium (when present) may be partly or wholly replaced by lanthanum, cerium, Misch metal and mixtures thereof, additionally, up to 10% of a material selected from the group consisting of platinum, tungsten, rhenium, silicon, tantalum and manganese may be added.

4. A structure as in Claim 1 having an adherent metallic bond coat between the substrate and the continuously graded layer.

5. A structure as in Claim 1 which contains up to about 20%, by volume, of porosity so as to accommodate swelling resulting from oxidation of the metallic constituent.

6. A structure as in claim 1 in which the graded layer is present in the form of discrete layers of essentially constant compoisition.

7. A structure as in claim 1 in which the deposited metallic particles have an aspect ratio of less than about 3:1.

8. A structure as in claim 1 in which the graded layer varies in essentially a continuous fashion from metallic to ceramic.

9. In a gas turbine engine air seal the type having a layer in which the composition varies from essentially 100% metal at one interface to essentially 100% ceramic at a second interface, and in which the stress state varies through the thickness, the improvement which comprises:

employing a ceramic material having an oxygen permeability constant which is less than about 10^{-8}gm cm^{-1} sec^{-1} at 1600°C and 50 Torr oxygen partial pressure as the ceramic constituent so that the metallic constituent is isolated and protected from oxygen and is thereby rendered more durable at elevated temperature under oxidizing conditions.

10. A seal as in Claim 9 in which the ceramic is selected from the group consisting of alumina, mullite and $MgO \cdot Al_2O_3$ spinel and mixtures thereof the metallic constituent is selected from the group consisting of the MCr materials where chromium ranges from about 20 to about 40%; the MCrAl materials where chromium

ranges from about 15 to about 45% and aluminum ranges from about 7 to about 15%; the MCrAlY materials where chromium ranges from about 15 to about 45%, aluminum ranges from about 7 to about 20% and yttrium ranges from about 0.1 to about 5%; and the MCrAlHf materials where chromium ranges from about 15 to about 45%, aluminum ranges from about 7 to about 15% and hafnium ranges from about 0.5 to about 7% in all of these materials "M" is selected from the group consisting of nickel, cobalt,iron and mixtures thereof with mixtures of nickel and cobalt being particularly favored, the yttrium (when present) may be partly or wholly replaced by lanthanum, cerium, Misch metal and mixtures thereof, additionally, up to 10% of a material selected from the group consisting of platinum, tungsten, rhenium, silicon, tantalum and manganese may be added.

11. A seal as in Claim 9 having an adherent metallic bond coat between the substrate and the continuously graded layer.

12. A seal as in Claim 9 having a layer of stablized zirconia on the free, ceramic, surface of the graded layer.

13. A seal as in Claim 9 in which the graded layer contains up to about 20%, by volume, of porosity so as to accommodate swelling resulting from oxidation of the metallic constituent.

14. A seal as in Claim 9 in which the ceramic material is alumina and the metallic material is MCrAlY.

15. A seal as in Claim 9 in which the ceramic material is alumina, the metallic material is an MCrAlY and in which there is a layer of porous, stabilized zirconia on the free, ceramic, surface of the graded layer.

16. A structure as in claim 9 in which the deposited metallic particles have an aspect ratio of less than about 3:1.

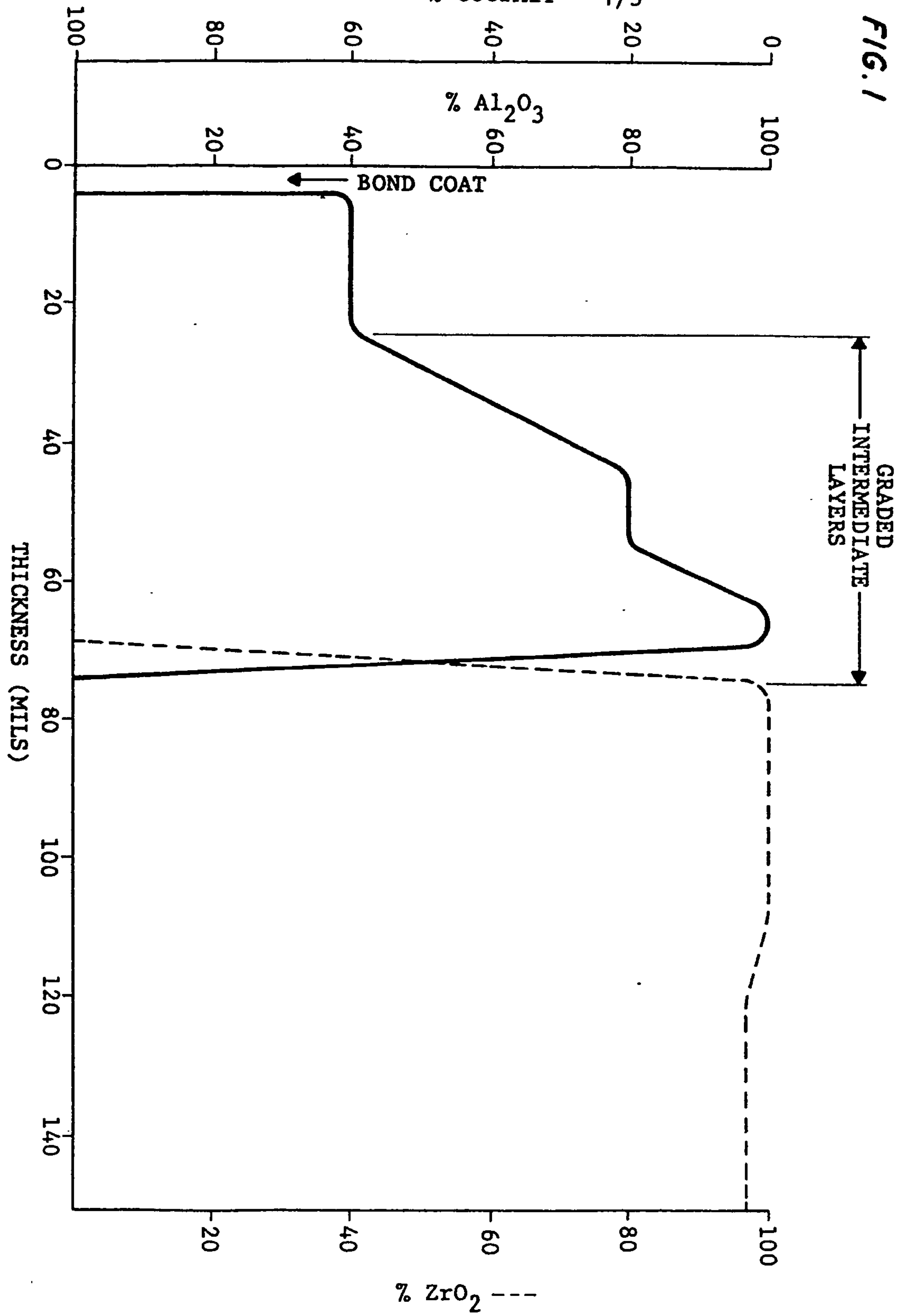
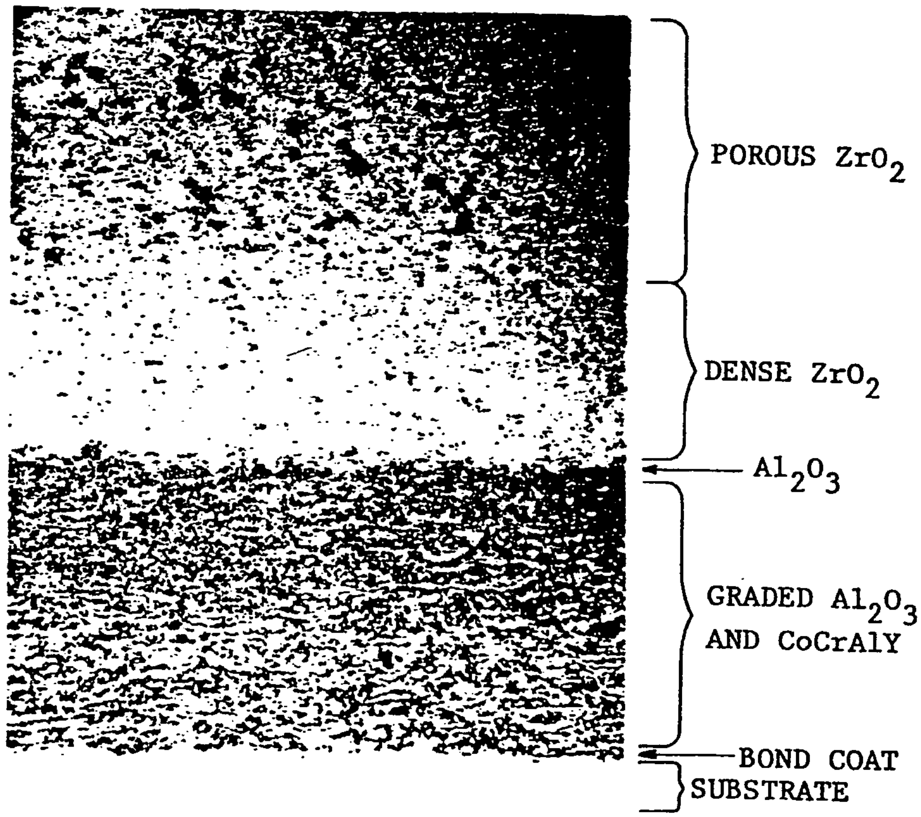

% CoCrAlY
100
80
60
40
20
0
% Al_2O_3
0
20
40
60
80
100
BOND COAT
GRADED INTERMEDIATE LAYERS
THICKNESS (MILS)
0
20
40
60
80
100
120
140
% ZrO_2 ---
20
40
60
80
100

FIG. 1

FIG. 2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DENSE ZrO_2
Al_2O_3
GRADED Al_2O_3 AND CoCrAlY
BOND COAT
SUBSTRATE

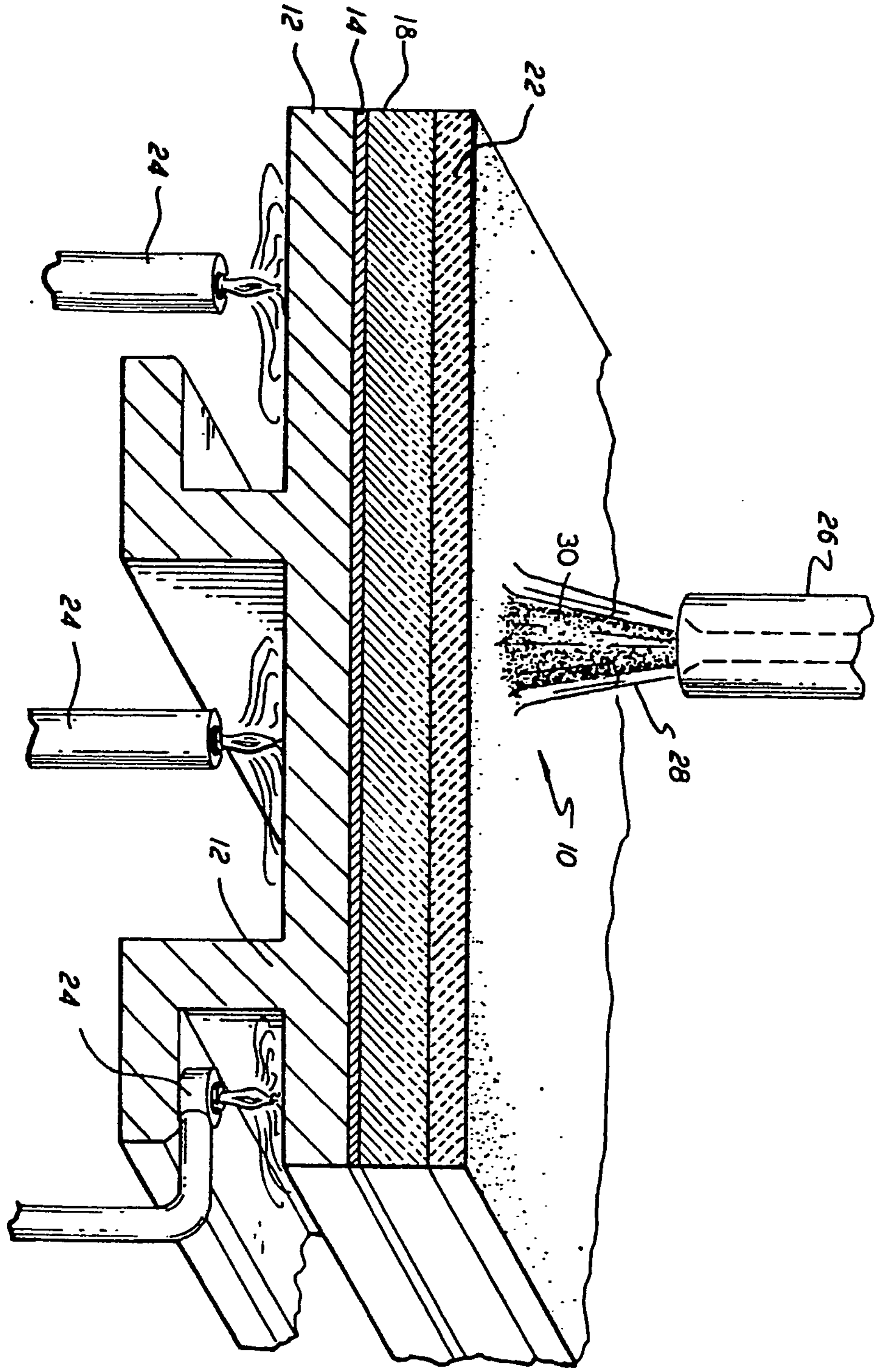

FIG.3

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FIG. 4

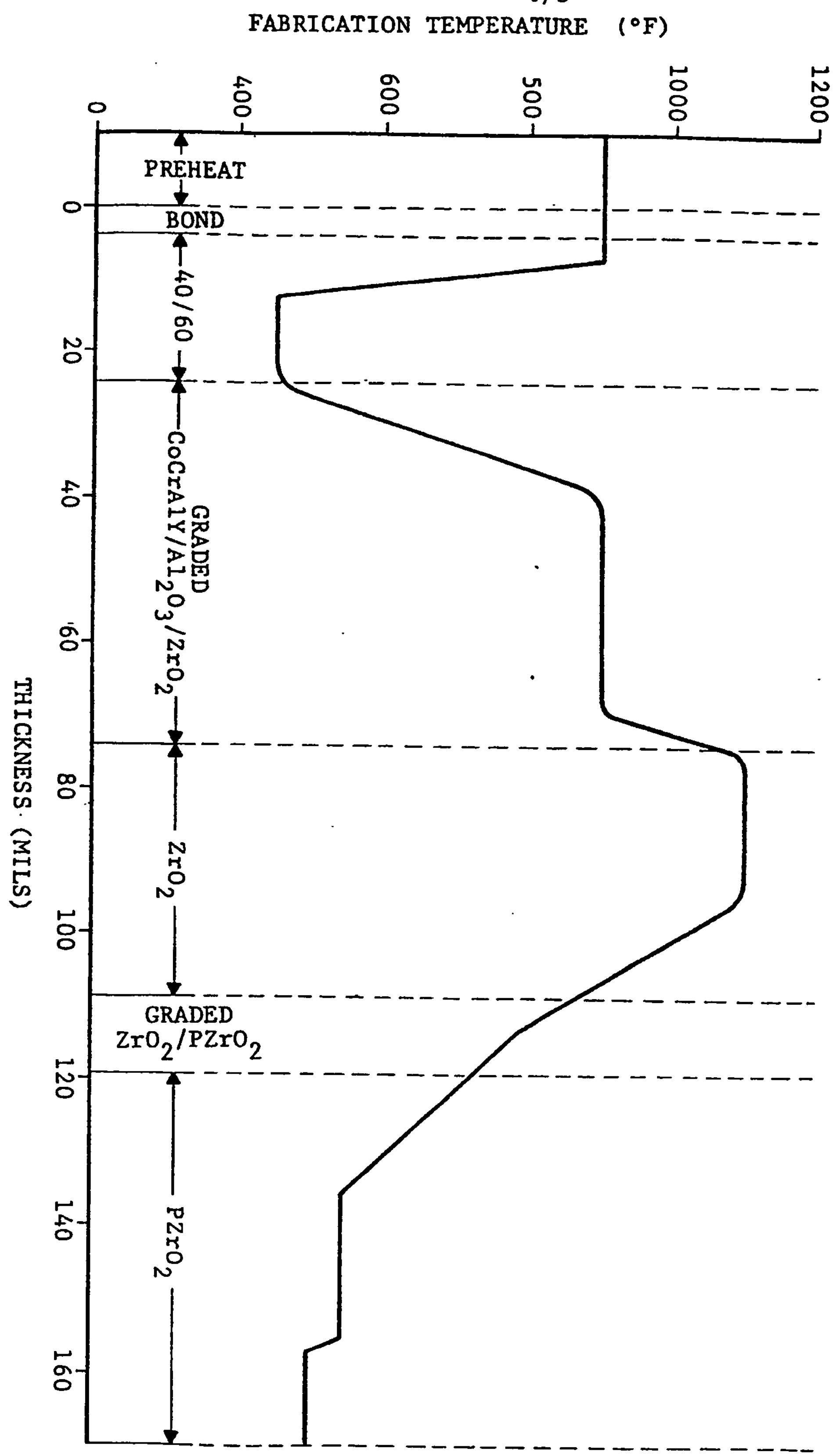
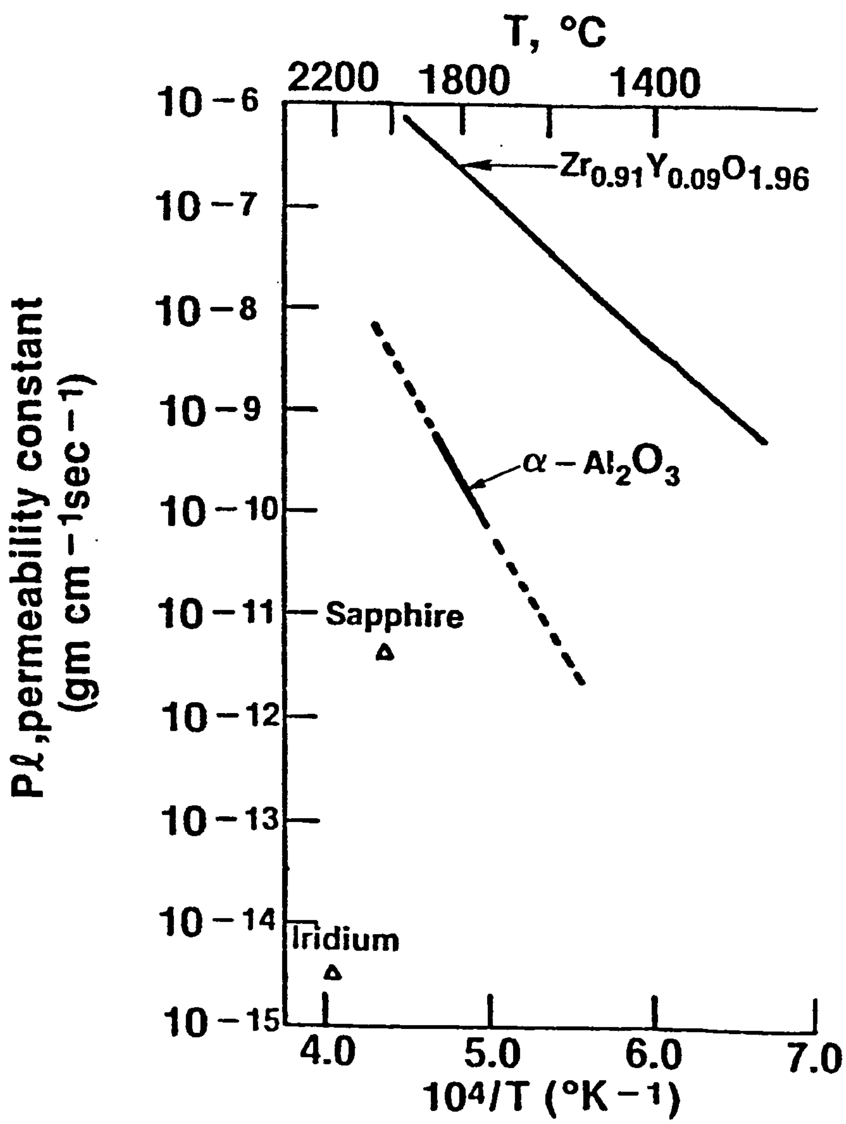


FIG. 5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10 −15
Zr0.91Y0.09O1.96
α − Al2O3
Sapphire
Iridium
4.0
5.0
6.0
7.0
10⁴/T (°K −1)
Pℓ, permeability constant
(gm cm −1sec −1)

European Patent Office

EUROPEAN SEARCH REPORT

0185603

Application number

EP 85 63 0204

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	FR-A- 918 141 (S.A. BROWN, BOVERI) * Claims 1-5; page 2, lines 53-54 *	1,2,8-10	C 23 C 4/10
X	PATENTS ABSTRACTS OF JAPAN, vol. 7, no. 139 (C-171)[1284], 17th June 1983; & JP - A - 58 52 469 (NIPPON KOKAN K.K.) 28-03-1983 * Abstract *	1-3,6, 8-10, 14,15	
A	PATENTS ABSTRACTS OF JAPAN, vol. 4, no. 174, 2nd December 1980; & JP - A - 55 113 880 (TOKYO SHIBAURA DENKI K.K.) 02-09-1980 * Abstract *	1,2,4, 6,9,10 ,11,14 ,15	
A	WO-A-8 201 898 (CASTOLIN) * Claims 1,12 *	1-3,6, 8,9,10 ,14,15	TECHNICAL FIELDS SEARCHED (Int. Cl.4) C 23 C F 01 D
A,D	US-A-3 091 548 (H.P. DILLON II) * Claims 1-5 *	1,2,4, 6,9,10	
A	US-A-3 758 233 (K.R. CROSS) * Claims 3,4; figure 3 *	1,2,4, 6,9,10	
	--- -/-		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	10-04-1986	ELSEN D.B.A.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	FR-A-2 190 754 (ASAHI GLASS CO.) * Claims 1,2,8,10,11-13 * ---	2,3,10-12	
A	SOVIET POWDER METALLURGY AND METAL CERAMICS, vol. 11, no. 3, March 1972, page 253, Consultants Bureau, New York, US; D.M. KARPINOS et al.: "Improving the adhesion of plasma-sprayed coatings to articles" * Page 253 * ---	1,2,4	
P,X	CH-A- 648 358 (CASTOLIN) * Claims 1,5 * -----	1-3,6, 8-10, 14,15	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

The present search report has been drawn up for all claims

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& : member of the same patent family, corresponding document